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Age Hardening of Copper-Aluminum Alloy Castings

Frank Randall

Randall, Frank

RANDALL AGE HARDENING OF COPPER-ALUMINUM ALLOY CASTINGS.

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Frank Randall

Butte, Montana

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A Thesis

Submitted to the Department of Metallurgy in Partial Fulfillment of the Requirements for the Degree of Bachelor of Science in Metallurgical Engineering

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Montana School of Mines

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AGE HARDENING OF COPPER-ALUMINUM ALLOY CASTINGS

INTRODUCTION

The phenomenon of age hardening was discovered by Wilm in 1906 in his investigations of the aluminum alloy, duralumin. He, however, did not arrive at any explanation for it. The first theory of age hardening was advanced by Merica, Waltenberg, and Scott(1) in 1919. These men worked on duralumin, also. Since 1919 there has been a great deal of work done on precipitation hardening, and there has been an enormous amount of literature written on the subject.

Age hardening of metals is of great commercial importance. Nearly all aluminum and magnesium alloys are given precipitation hardening treatments, especially those used in aircraft. Merica(2) list 106 age hardening systems, many containing several alloys that will respond to this type of treatment.

MECHANICS OF AGE HARDENING

Age hardening occurs in alloys of the solid solution type containing a hardening constituent, be it metal or metallic compound, which is more soluble in the solvent phase at higher temperatures than at lower ones. The solid solution, saturated with respect to the hardening constituent, if rapidly cooled or quenched to lower temperatures, is supersaturated, and unstable. If the alloy is allowed to stand at the quenching temperature, or some higher one, below that required for one solid solution to exist, there will be a precipitation of the hardening constituent. The fine precipitate formed at the potential slip planes of the alloy obstructs slip, and this automatically causes hardening.

In the original theory of Merica, Waltenberg, and Scott[1] the following four points were advanced for the age hardening of copper-aluminum alloys:

1. Age hardening is possible because of the solubility relations of the hardening constituent in the aluminum (Figure 1 - from Dix and Richardson[3]).

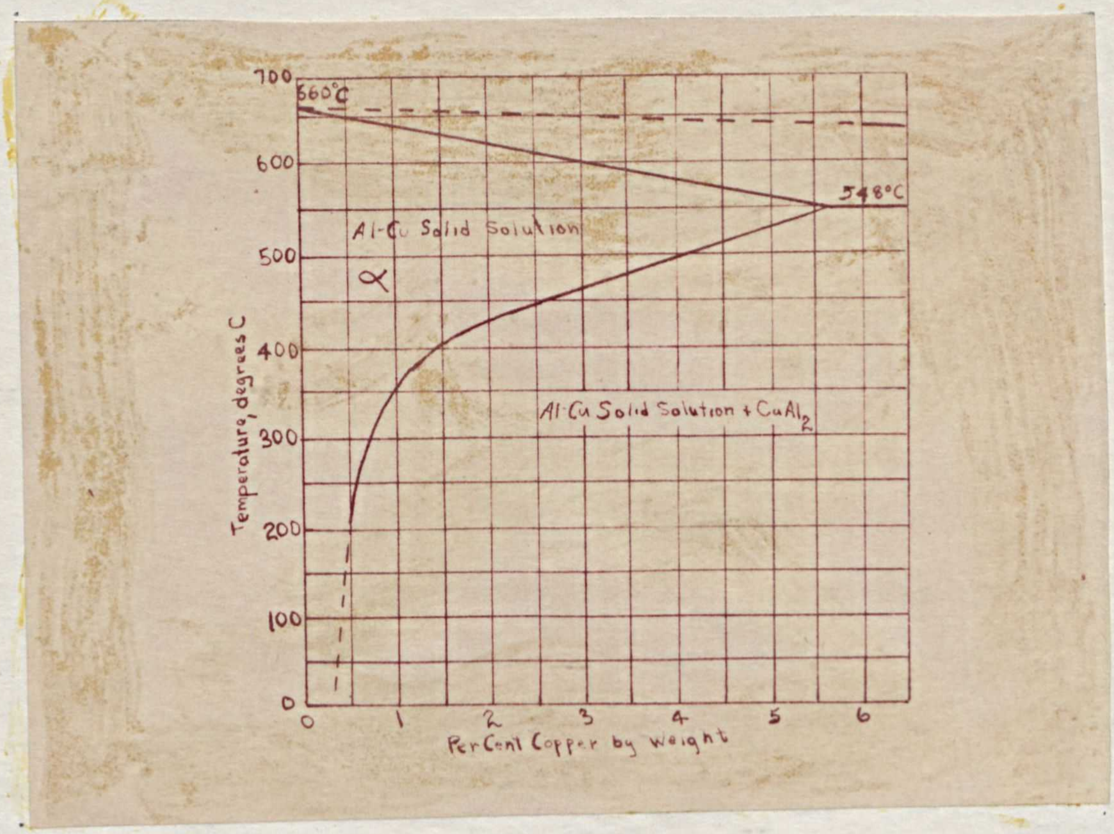

Figure 1. - Aluminum End of the Cu-Al Diagram.

2. The hardening constituent is $CuAl_2$.

3. Hardening is caused by the precipitation of this constituent is some form other than atomic dispersion, and probably in some fine disperse, molecular, colloidal, or crystalline form.

4. The hardening effect of $CuAl_2$ is related to its particle size.

This last statement was included to account for the fact that during aging the alloys would harden steadily for a while, reach a maximum hardness, and then soften. Merica explained this effect of particle size on hardness by saying that during hardening the precipitate particles forming first would be very small, and might not cause much hardening, whereas larger particles would be more effective; still larger particles falling off in effectiveness. He thought that the large particles were less effective because there were less of then to key the slip planes together. Figure 2, taken from his article[(2)] shows this effect.

Later work has thrown some doubt on this "critical particle size" theory. For example, alloys age hardened at low temperatures reach maximum hardness without precipitation of particles large enough to be resolved with a microscope. (Dix and Richardson[(3)], and Fink, Willey, and Smith[(4)] found that streaks form on the surface of the alloys during room temperature aging. These are taken as evidence of the presence of very small

Conceptions of the Effect
Of Particle Size and Number
On the Hardening Power
Of a Constant Amount
Of Hardening Phase

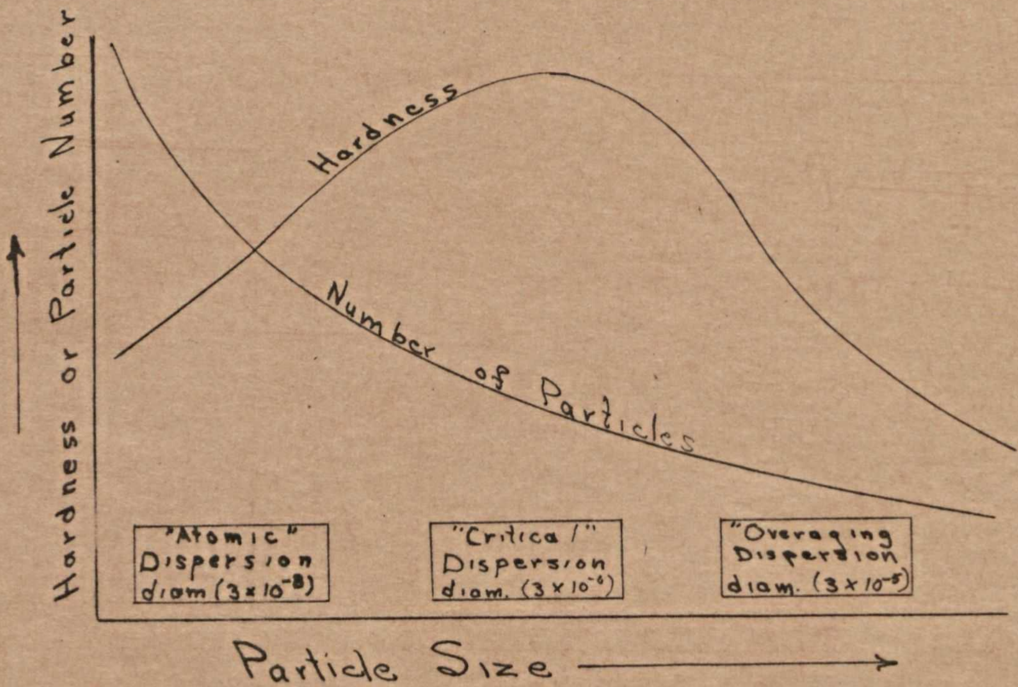

Figure 2

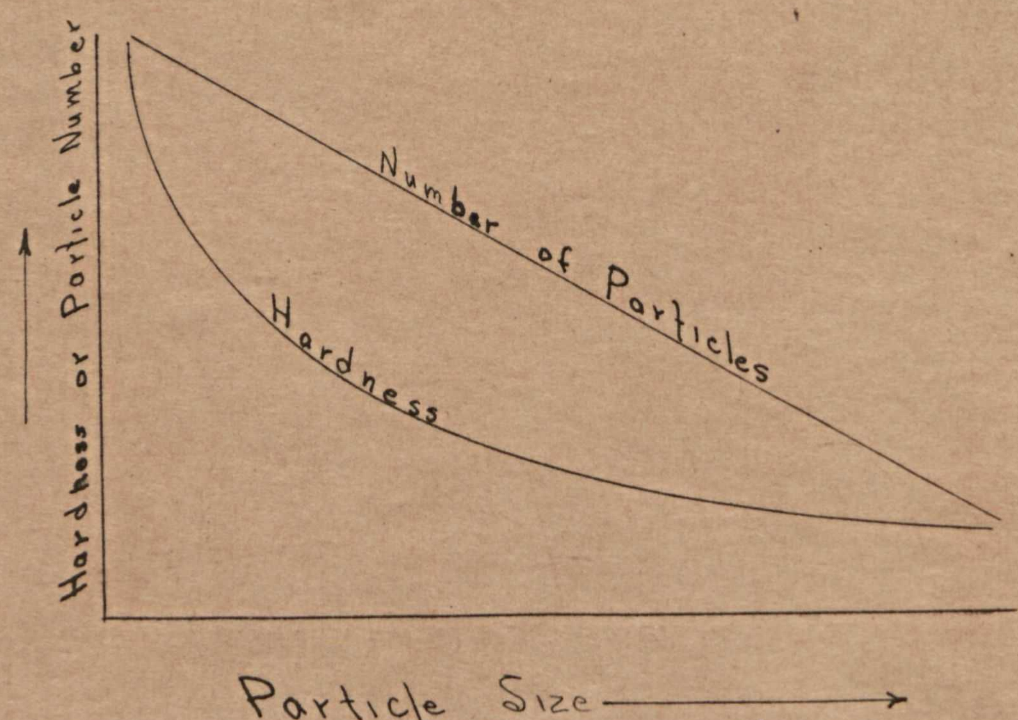

Figure 3

f. r.

precipitate particles). Aging at elevated temperatures, on the other hand, yields $CuAl_2$ particles of resolvable size, at maximum hardness. This, in my opinion, is incompatible with the "critical particle size" theory which requires that there be a certain size of particles for maximum hardness. Another theory is graphically summarized in Figure 3. According to this view, it is the number of particles per unit volume that above all else determines the hardening effect, with the smallest conceivable unit of precipitate being the most effective form. This theory does not apparently account for the initial rise in the hardness curve. However, on closer consideration this can be explained as follows; maximum hardness is obtained with the smallest possible particles; but, nucleation and grain growth are slow enough so that when there is a maximum number of these small particles formed there will be some that have grown to a larger size; the larger particles tend to soften the alloy, and the smaller ones tend to harden it; therefore, there will be a time when these two opposing tendencies will reach a balance giving maximum hardness, if the rate of nucleation is greater than the rate of grain growth.

One universal feature of aging is quite clear; prolonged aging causes continued coalescence of the precipitate particles, and results in a relatively few segregations of relatively large size, their number and disposition being insufficient to cause great hardness. The alloy is then termed "over aged".

The optimum development of age hardening is then to be expected when:

1. The hardening constituent is effective in resisting or preventing slip. (Merica[2] says that the hardness of the precipitated phase has little effect on the attainable hardness of the alloy).

2. When the volume of the segregated constituent is large.

3. When the segregated particles are very small and numerous.

OBJECT OF THE INVESTIGATION

The age hardening behavior of high aluminum alloy castings of copper and aluminum was chosen as the problem to be studied. Many investigations have been carried out on alloys cold rolled prior to solution heat treatment, but very little has been done on castings.

An attempt was made to determine the effect of the following variables on the age hardening properties:

1. The amount of copper in the alloy.

2. The amount of strain the casting received before solution heat treatment.

3. The age hardening time.

4. The age hardening temperature.

The solution heat treatment and the subsequent quench were as nearly the same for all alloys as possible.

PREPARATION OF SAMPLES

Samples were prepared of aluminum pellets and copper sheet, both of high purity. Melting of the metals was done in a clay crucible in an electric resistance furnace. Copper was melted first, and the aluminum pellets poured in on top of the molten copper. As soon as melting was completed the alloy was stirred thoroughly and poured. No flux was used to cover the melts, but they were protected by a thin layer of coke dust. Alloys were made of these compositions:

Copper	Aluminum
.8%	Balance
1.1%	"
3.3%	"
3.5%	"
3.7%	"
3.9%	"
4.0%	"
4.5%	"
5.8%	"

(These compositions are given in weight per cent).

The castings were quenched from the molten state in (a) air, (b) boiling water, and (c) cold water (13°C). Some of the air quenched castings were given a 10 per cent cold roll, others a 50 per cent cold roll, and the rest were not given any treatment before solution annealing.

Each bar was sawed into five equal pieces about a half an inch wide. (The dimensions of the bars, in inches, were ½ by 1¼ by 3). The exact size in each casting varying with the amount of imperfect material on the top. These tops, which were very porous, and contained relatively large amounts of Al_2O_3 and coke, were discarded.

The small bars were given a solution heat treatment at 535-545°C for two hours, and quenched in cold water to about 15°C.

EXPERIMENTAL PROCEDURE

Five sets of samples for age hardening tests were taken. Each consisted of alloys of all compositions and treatments. One set was tested to get the hardness before hardening had started. Of the four remaining groups, one was allowed to age at room temperature, another at 85°C in a water bath, another at 170°C in an electric oven, and the last in an electric furnace at 300° ± 10°C. The samples were quenched in water to approximately room temperature, and tested for hardness after 4, 16, 25, 36, 49½, 70, and 102 hours elapsed time. Hardness was measured with a Rockwell superficial hardness tester, using a 1/16 inch ball penetrator, and a fifteen kilogram major load.

Since the castings were not entirely uniform, the hardness of any sample varied considerably over its entire surface, but in a small area the readings were quite consistent. Five small areas near the center of each sample were outlined, and the readings taken in each of these areas in every test. Usually five readings - never less than three - were taken on each sample, and the values averaged.

It took over two hours to run hardness tests on all of the bars, and during this time the alloys were aging at room temperature. This probably had some effect on the hardening, but I have no idea of its magnitude or disposition.

RESULTS AND DISCUSSION

Since tabulations of the data obtained are of little inerest or importance they were omitted from this paper. All pertinent data has been incorporated into the accompanying graphs. Only typical curves, or those definitely having some significance, are included.

Effect of the Amount of Copper in the Alloy-- The maximum hardness attainable increases rapidly with the amount of copper present from 1.1 per cent up to about 3.7 per cent.

Above 3.7 per cent the rate of increase drops off. Figure 4 shows this relation in alloys that were quenched from the molten state in hot water, solution heat treated two hours at 535-545°C, requenched to 15°C in cold water, and aged at various temperatures. That the hardness should increase with the amount of copper present is to be expected, but the reason for the drop in the rate of hardness increase is not so obvious. It must be due to the alloy's approaching saturation in the hardening phase.

The work of Kempf[5], and Brick and Phillips[6] shows hardness increasing up to the saturation composition of alpha solid solution (Figure 1), or 5.4 per cent copper. In some of my alloys, however, the hardness appears to be still increasing with the amount of copper. Since the solution heat treatment time was short, all of the $CuAl_2$ may not have gone into solution. If this were true the castings may have acted as though only the amount of copper in solution were present. This may have happened with my 5.8 per cent copper alloys.

One interesting thing is proved - it is possible to age harden alloys containing more copper than the saturated composition of any alpha solid solution (Figures 1 and 4).

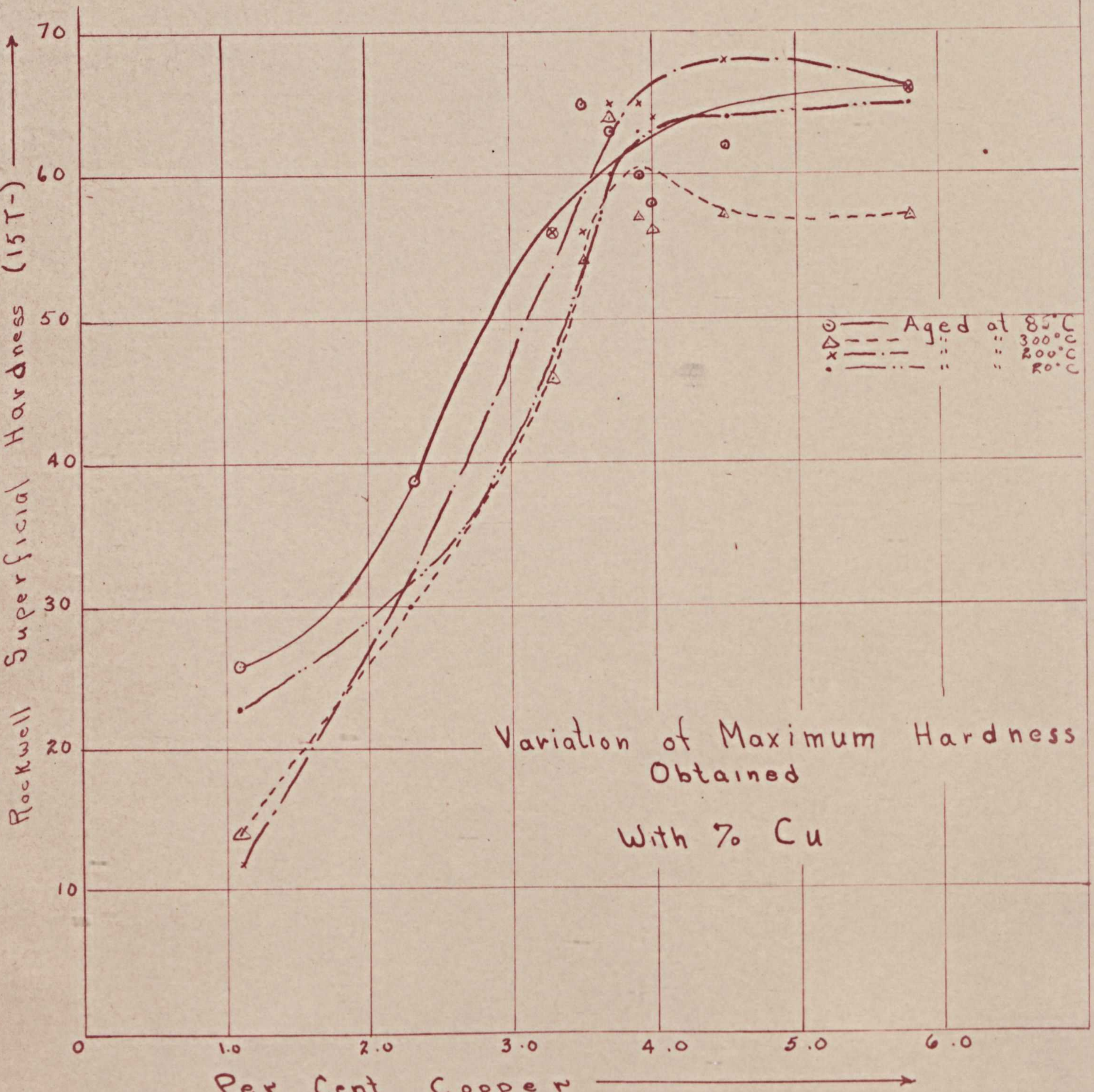
Rockwell Superficial Hardness (15T-)
70
60
50
40
30
20
10
0
1.0
2.0
3.0
4.0
5.0
6.0
Per Cent Copper
Aged at 85°C
300°C
200°C
20°C
Variation of Maximum Hardness Obtained
With % Cu

Figure 4

Effect of Age Hardening Temperature on Maximum Hardness of Cast Al-Cu Alloys

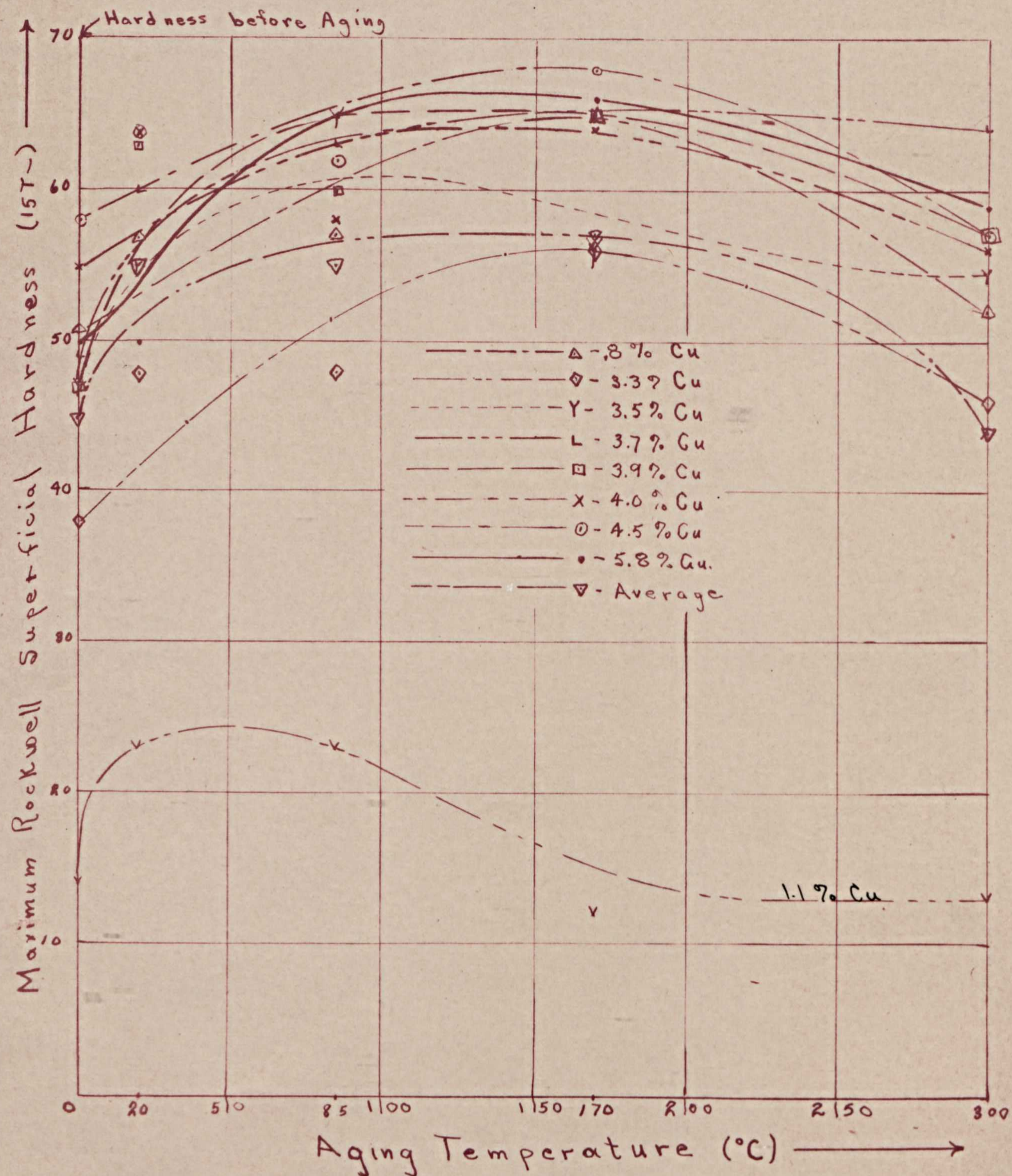

Figure 5

Effect of Aging Temperature-- Figure 5 shows the effect of the precipitation heat treatment temperature on the maximum hardness attained with alloys of various compositions. The maximum hardness increased with temperature at first, and in all but two cases reached a maximum between 100°C and 200°C. At still higher aging temperatures the maximum hardness decreased. These phenomena are probably related in some way to the rates of nucleation and grain growth of $CuAl_2$.

Double Aging Peaks and Effect of Strain-- Nearly all of the alloys exhibited two peaks in their hardening curves. This was most pronounced in the 3.3 per cent copper alloys originally quenched in hot water (Figure 6). In alloys containing 3.5 per cent copper, air quenched until solid, then in water , and cold rolled 50 per cent (Figure 7) the first peaks were very small. They were absent in the 1.1 per cent copper alloys quenched in air, and cold rolled 10 per cent (Figure 8).

Fink and Smith[7] have explained that double peaks are due to the effects of strain. It is known that strain produces plastic deformation[8]. It is also known that plastic deformation accelerates the rate of precipitation[8] of the hardening constituent. If the plastic deformation occurs locally at grain boundaries and along slip planes, as would be expected, precipitation

Typical Age Hardening Curves
Molten Castings Quenched In Hot Water
And
Given Same Solution Heat Treatment
As All Other Alloys

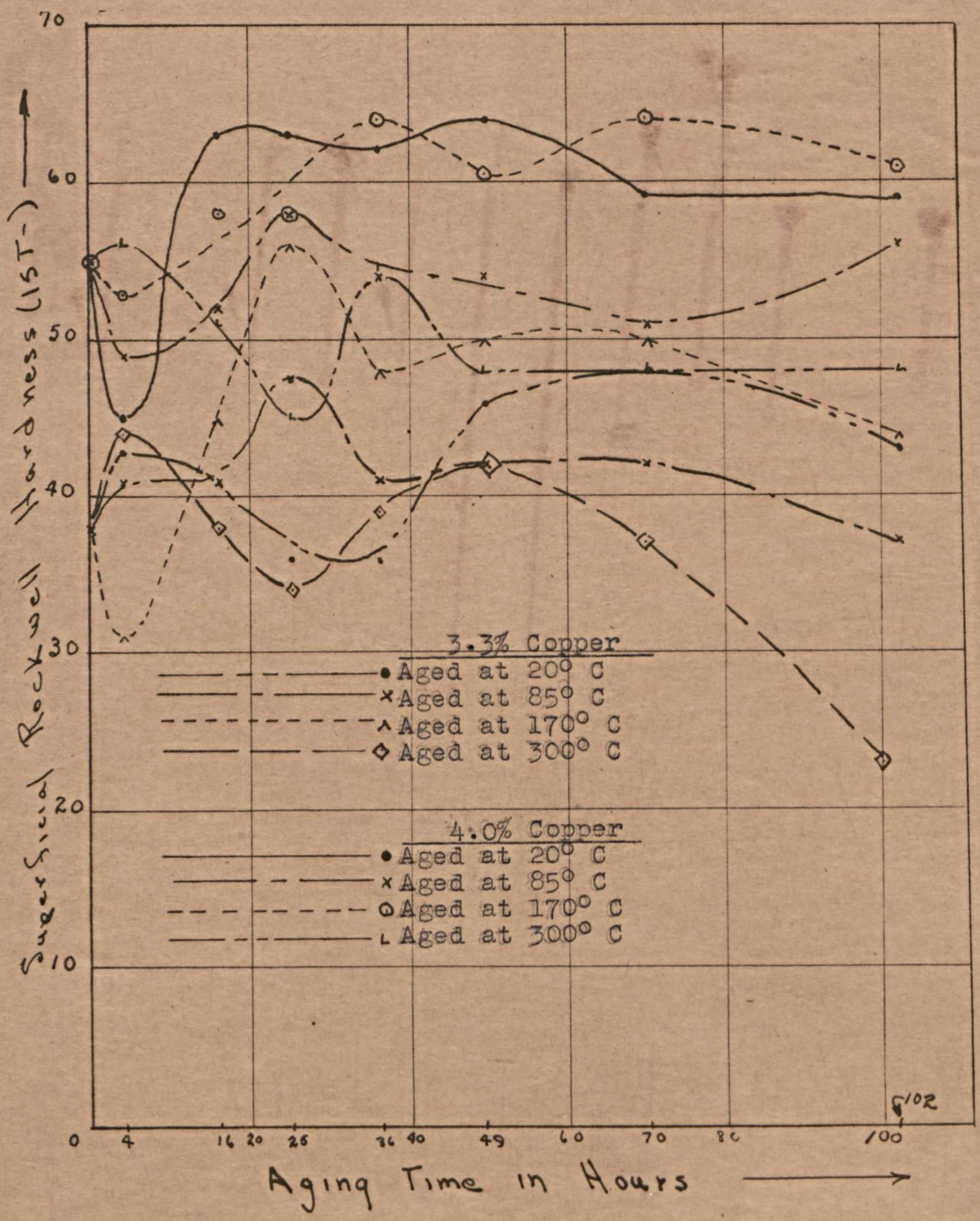

Figure 6

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Age Hardening Curves
3.5% Copper Alloy
Molten Metal Air Quenched Until Solid,
Then Quenched In Cold Water
Given Same Solution Heat Treatment
As All Other Alloys
After 50% Cold Roll

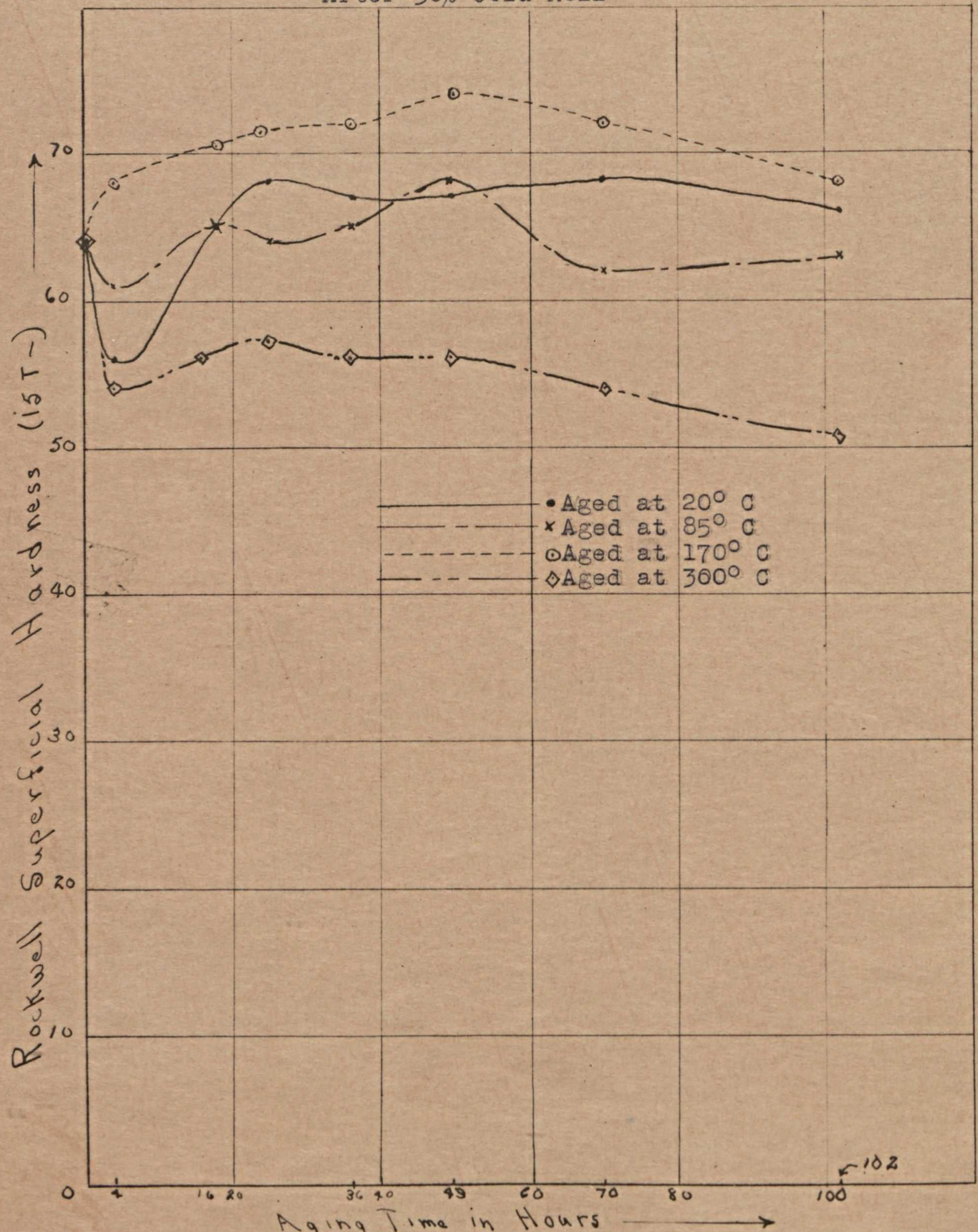

Figure 7

would occur at different rates in different parts of a given grain. The deformed areas should, therefore, harden at a different rate than the undeformed places, and ordinary macroscopic methods of measuring hardness should yield an integrated curve. Since such a curve is obtained this explanation seems valid, at least for alloys strained after solution heat treatment. The alloys tested were thermally strained by the quench from the solution heat treatment temperature, but their behaviors on aging were very different. These differences must have been due to the thermal or mechanical strain they received before the anneal. Why these pre-anneal strains should effect the age hardening is not clear. It may be due to grain refinement, or changes in the rate of nucleation of the $CuAl_2$. From examination of Figures 6, 7, 8, 9, 10, and 11 it seems that: (a) the magnitude of the first maximum increases with the strain given the alloy, (b) the time necessary to attain the first maximum on the hardness curve increases with increased thermal strain, (c) the time necessary to attain the first maximum is not changed by varying the cold rolling strain, and (d) the maximum hardness increases with the strain of either type.

The alloys originally quenched in cold water tended to show three age hardening peaks, especially those containing 3.9 per cent copper (Figure 9).

Typical Age Hardening Curves
Of Castings Cooled In Air
Solution Heat Treated
at 535-545° C
Quenched to 15°C In Cold Water

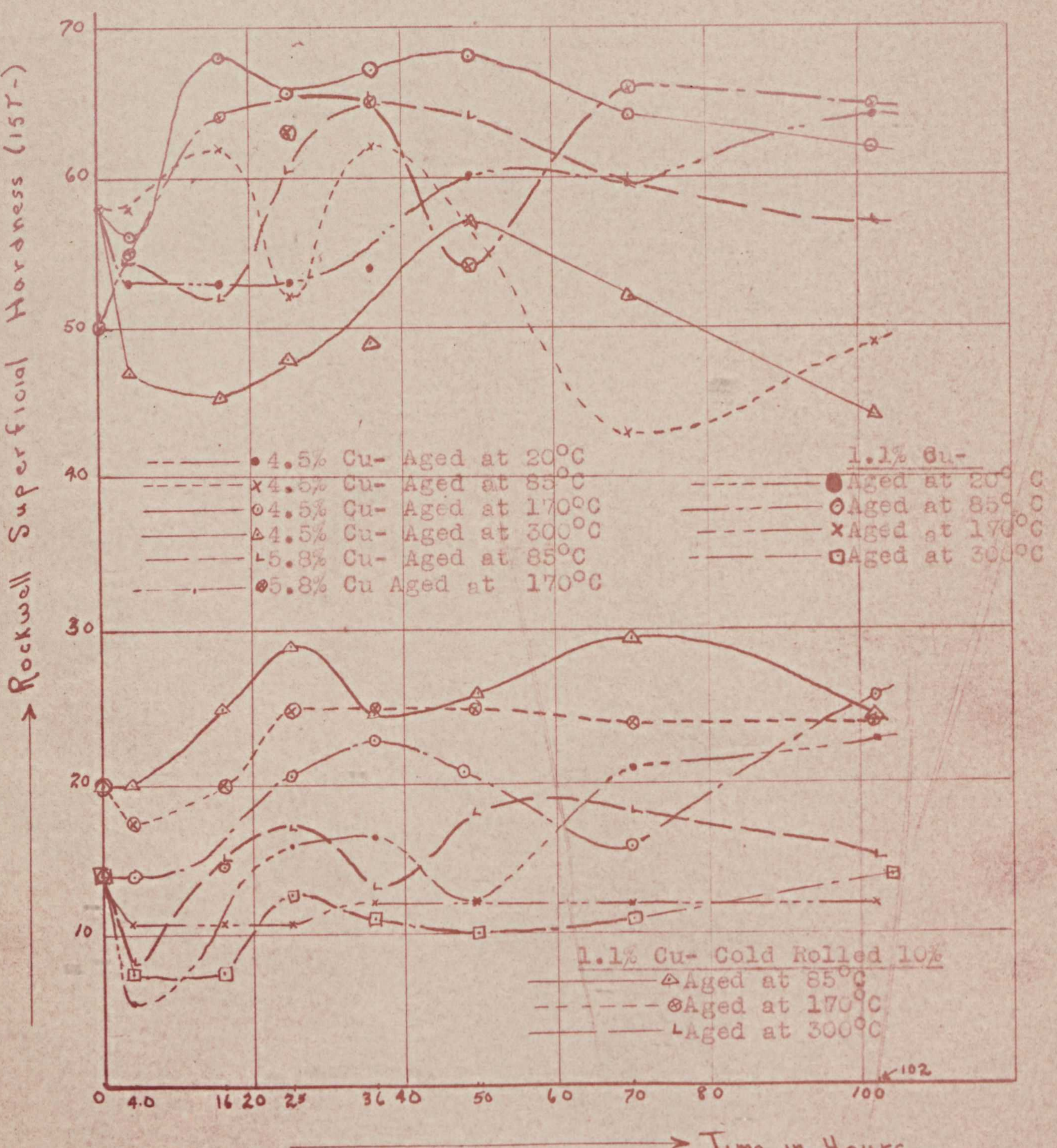

Figure 8

Typical Age Hardening Curves
Molten Castings Quenched In Cold Water
And
Given Same Solution Heat Treatment
As All Other Alloys

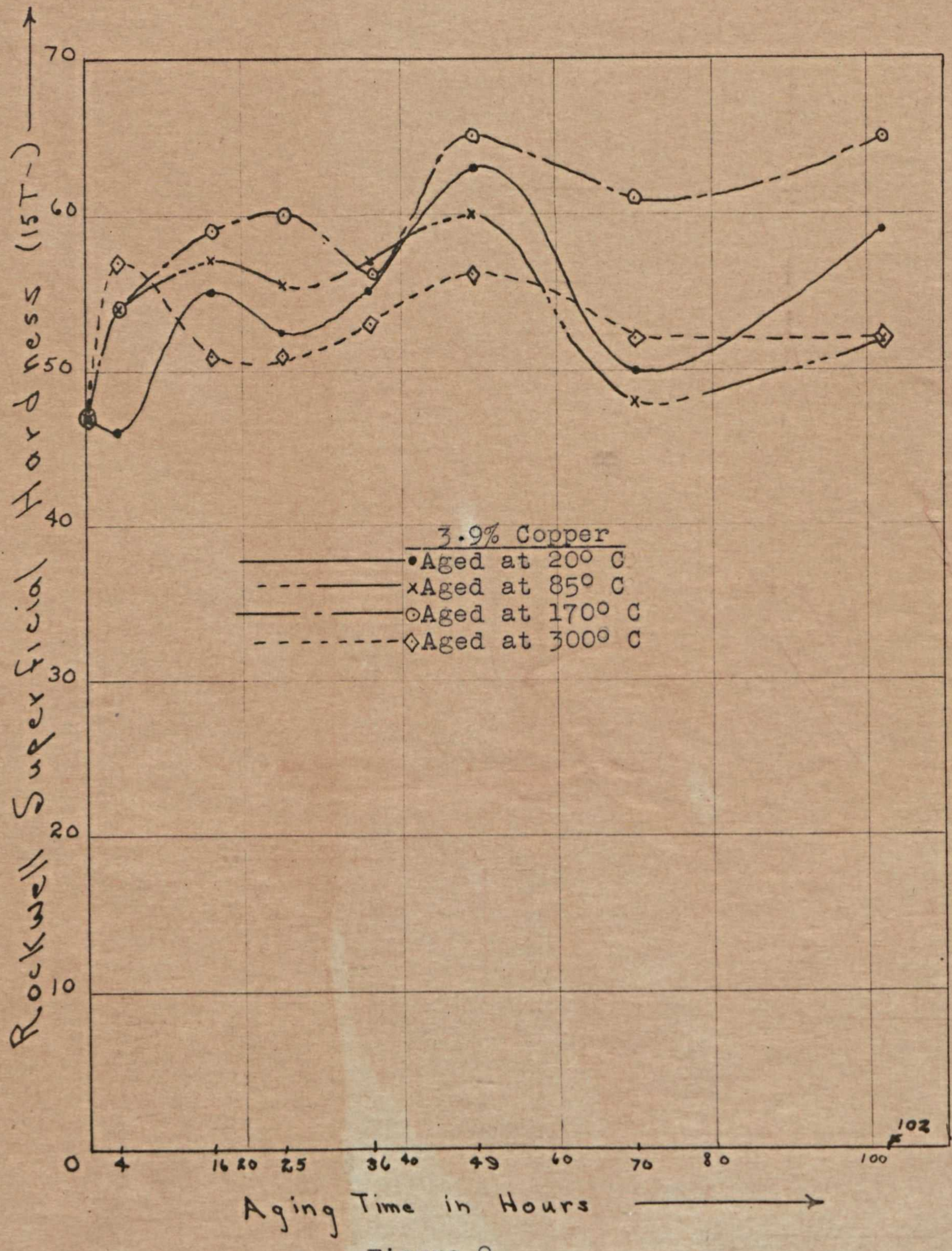

Figure 9

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Typical Age Hardening Curves
Of Castings Cooled In Air
Solution Heat Treated
at 535-545° C
Quenched to 15° C In Cold Water
3.5% Copper

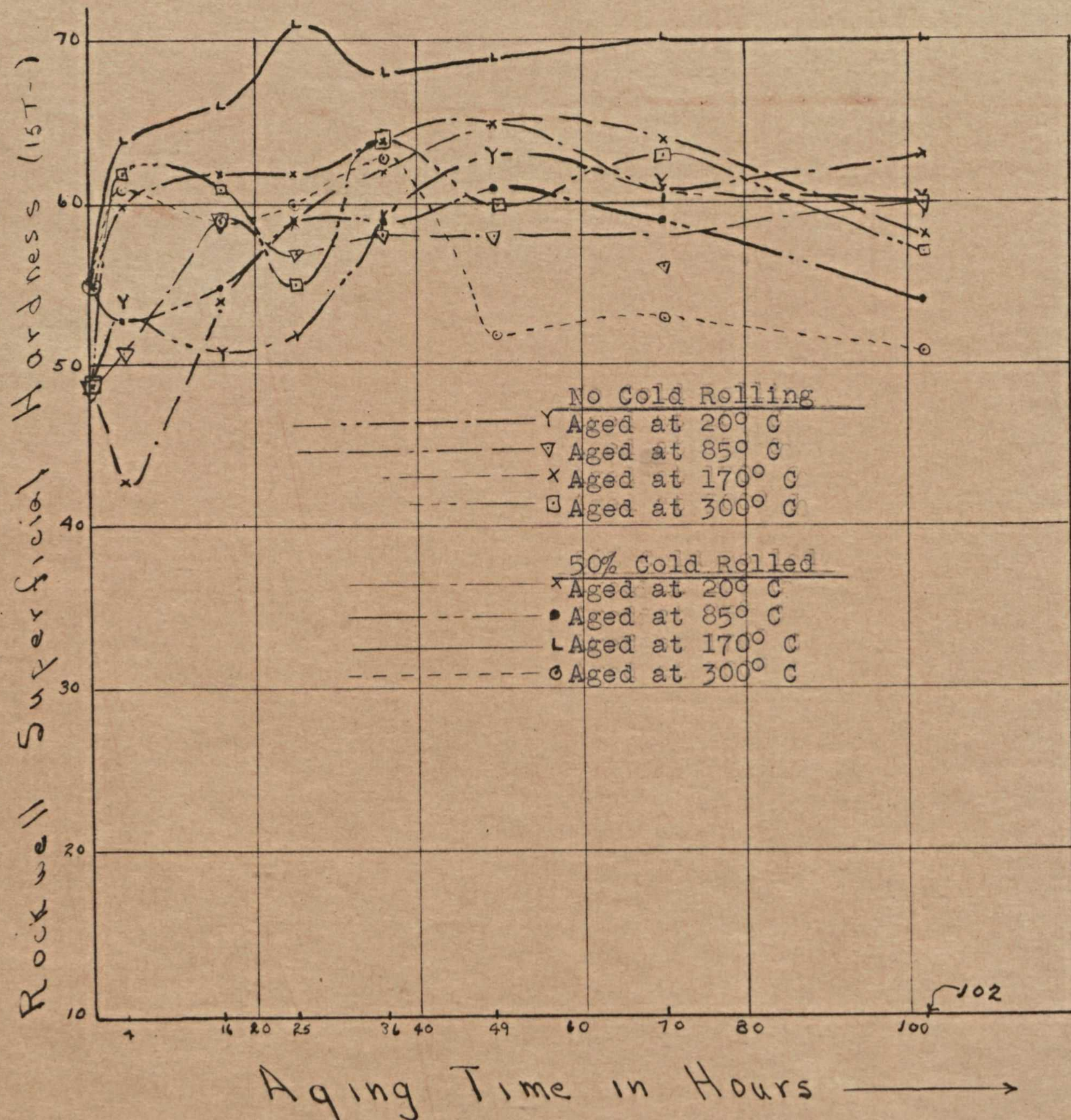

Figure 10

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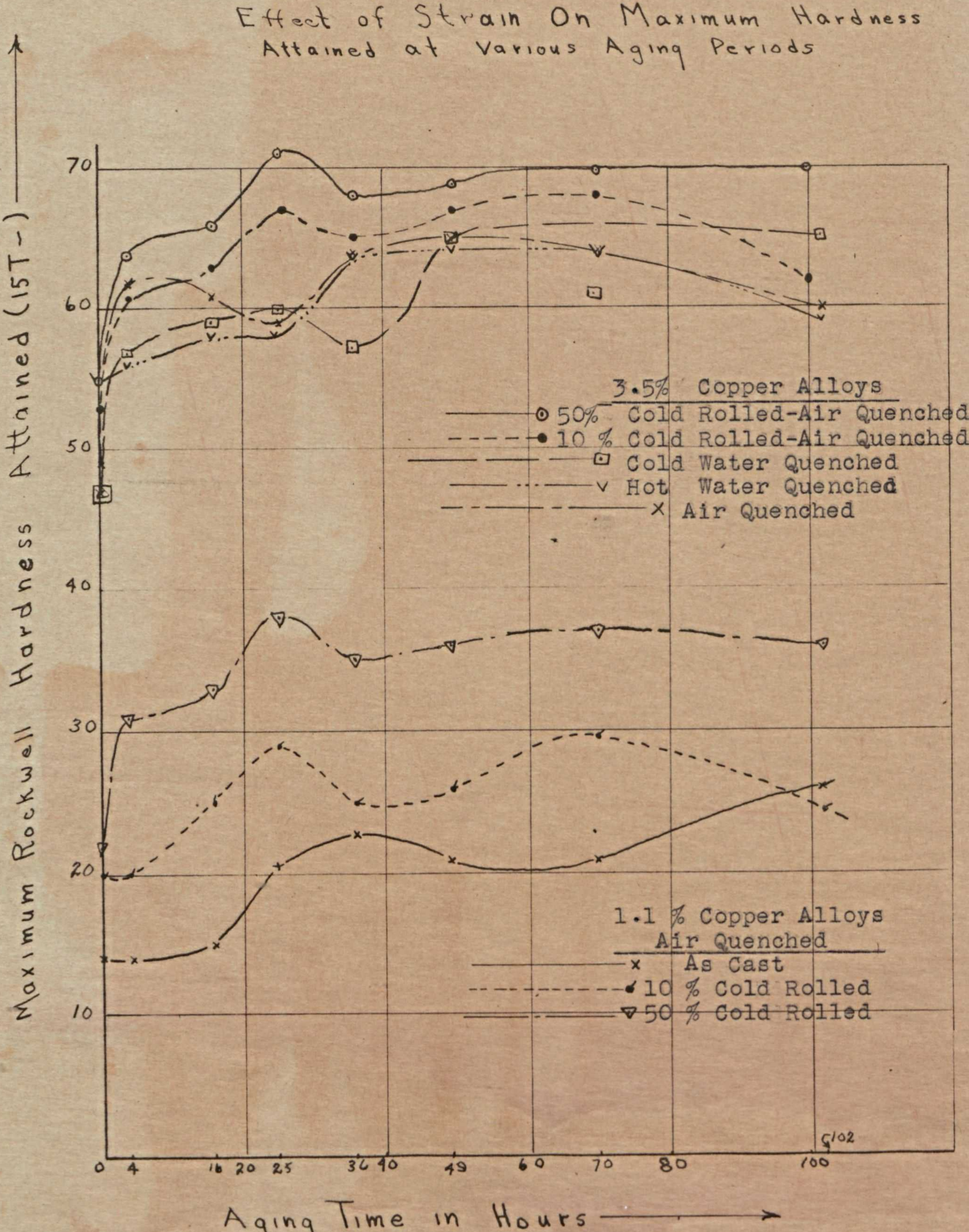
Effect of Strain On Maximum Hardness
Attained at Various Aging Periods
Maximum Rockwell Hardness Attained (15T-)
70
60
50
40
30
20
10
0
4
16
20
25
36
40
49
60
70
80
100
3.5% Copper Alloys
50% Cold Rolled-Air Quenched
10 % Cold Rolled-Air Quenched
Cold Water Quenched
Hot Water Quenched
Air Quenched
1.1 % Copper Alloys
Air Quenched
As Cast
10 % Cold Rolled
50 % Cold Rolled
Aging Time in Hours

Figure 11

Best Aging Alloys-- The greatest increases in hardness were obtained with two different alloys. One was a 3.3 per cent copper alloy, originally quenched in boiling water, and aged at 170° for 25 hours (Figure 6). The other contained 3.9 per cent copper, was quenched in cold water, and aged at 170°C (Figure 9). This alloy developed its maximum hardness twice - after 49½ hours and after 102 hours. In both of these alloys the increase in Rockwell superficial hardness was 18 points.

The hardest of the thermally strained alloys contained 4.5 per cent copper. It was originally cooled in air, and the aging temperature was 170°C. Maximum hardness was reached after precipitation heat treatments of 16 and 49½ hours (Figure 8).

The alloy quenched in air, cold rolled 50 per cent, and containing 3.5 per cent copper, reached the greatest hardness of any mechanically strained alloy. It was aged at 170°C for 25 hours. (Figure 10).

CONCLUSIONS

1. Copper-aluminum castings may be successfully age hardened without being mechanically strained.

2. In the composition range .8 to 5.8 per cent copper, the maximum hardness attainable of copper-aluminum alloys increases with the amount of copper present.

3. It is possible to age harden alloys containing more copper than any saturated alpha copper-aluminum solid solution.

4. There is an aging temperature range, above or below which the alloys will not develop their maximum hardness.

5. On aging, copper-aluminum alloys tend to develop two or more hardening peaks.

6. Thermal strain before solution heat treatment raises the magnitude of the maximum of hardness attainable, and delays the first and second maxima.

7. Mechanical strain before solution heat treatment increases the maximum hardness obtainable by aging.

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NOTE: The book "Age Hardening of Metals", published by the American Society for Metals, lists 1033 references on age hardening and closely related subjects.